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"Modification of Fluoropolymer Surfaces with Electronically Conductive Polymers

by

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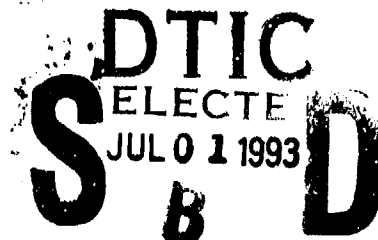
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# Modification of Fluoropolymer Surfaces With Electronically Conductive Polymers

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## ABSTRACT

We describe methods for coating fluoropolymer surfaces with thin films of electronically conductive polymers. Modification of the fluoropolymer surface prior to coating with conductive polymer is necessary to achieve good adhesion between the fluoropolymer membrane and the conductive polymer coating. We describe four different procedures for modifying the fluoropolymer surface so as to promote strong adhesion. These procedures are based on a wet chemical treatment of the fluoropolymer or on exposure of the fluoropolymer surface to a hydrogen plasma, an ultraviolet laser, or an electron beam. Finally, we show that it is possible to "write" patterns with the conductive polymer onto the fluoropolymer surface.

## INTRODUCTION

The ability to render insulating materials (eg. polymers) conductive is important for many technological applications, including EMI-RFI shielding [1] and antistatic coatings [2]. Polymers are most often rendered conductive by loading with conductive particles or by applying conductive metal coatings [3]. During the last ten years, a variety of polymers, that are themselves electronically conductive, have been discovered and investigated [4]. These inherently-conductive polymers provide an alternative route for rendering conventional, insulating, plastics conductive.

In some cases conventional solution-based film-coating methods can be used to coat insulating plastic surfaces with electronically conductive polymers [5]. However, most conductive polymers are insoluble in all solvents. Insulating plastics and fabrics can be coated with thin films of these polymers by polymerizing the conductive polymer directly onto the surface of the desired insulating substrate [6-11]. If this approach is to work, there must be a strong adhesive interaction between the conductive polymer film and the underlying insulating-polymer surface. Fortunately, conductive polymers such as polypyrrole adhere quite well to many substrates, including nylon, polycarbonate, cellulose, polyester, and quartz [6-11].

We have found, however, that the adhesion between conductive polymers and fluoropolymers is quite poor. This is not surprising since the adhesion between fluoropolymers and most other materials is generally poor [12]. A variety of techniques for modifying fluoropolymers to improve the adhesion of metal coatings have been developed [12]. These include chemical methods [13], plasma treatments

[12], and electron beam irradiation [14]. We have explored some of these surface modification procedures as a means to improve the adhesion between fluoropolymers and electronically conductive polymers. We show in this paper that strongly-adherent thin films of various conductive polymer can be synthesized onto such modified fluoropolymer surfaces. We also show that by spatially-controlling the area that is modified, patterned conductive polymer coatings can be prepared.

## EXPERIMENTAL

*Materials.* Poly(tetrafluoroethylene) (PTFE) (10 mil sheet, Cadillac Plastic) and Poly(tetrafluoroethylene-co-hexfluoropropylene) (FEP) (10 mil sheet, donated by Dupont) were degreased by ultrasonication in methylene chloride. Pyrrole, N-methylpyrrole, 3-methylthiophene and aniline (the monomeric precursors to the conductive polymers) were obtained from Aldrich and were distilled under nitrogen prior to use. Tetrahydrofuran (THF) was distilled from sodium benzophenone. Deionized water (18 Mohm) was prepared by passing distilled water through a Millipore Milli-Q purification system. All other reagents were used as received.

*Equipment.* A custom-made, disk-shaped hydrogen plasma system, utilizing a ring cathode [15] and a soft-vacuum pulsed electron-beam source [16] was used for plasma treatment of the fluoropolymer surfaces. A XeCl Excimer Laser (Lumonics HyperEX-400) was used for phototreatment of the fluoropolymers. X-ray photoelectron spectroscopy (XPS) was performed using a Perkin Elmer 5500 ESCA spectrometer using a 300 W Mg source at 15kV and an Apollo 3500 Computer. A flood gun was used to neutralize sample charging. Contact angle measurements were

obtained with a Rame-Hart model 100A telescopic goniometer.

Ultraviolet-visible-near-infrared (UV-vis-NIR) spectra were obtained with a Hitachi U-3501 spectrometer. Scanning electron micrographs were obtained using a Phillips 505 microscope with a  $\text{LaB}_6$  source. Conductivity measurements were made with a conventional four point probe system built in house [17].

*Modification of the fluoropolymer surfaces.* Four different surface modification methods were explored. These methods are based on a wet chemical treatment of the fluoropolymer or on exposure of the surface to a hydrogen plasma, an ultraviolet laser, or an electron beam. The wet chemical method was developed by Shoichet and McCarthy and results in carboxylation of the fluoropolymer surface [18]. Briefly, the surface of the polymer was first reduced using a THF solution of sodium naphthalide (0.12 M). This reduction was done at 0°C for 10 minutes. The reduced surface was then oxidized by exposure to a solution of potassium chlorate in sulfuric acid (0.16M) for two hours at room temperature. The hydrogen plasma method entails exposing the fluoropolymer to the downstream near afterglow of a DC hydrogen discharge. The discharge was operated using 0.3 Torr of hydrogen gas and a 100 mA current to form a disk-shaped plasma 7 cm in diameter and an afterglow 1 cm thick. The samples were placed 0.63 cm from the plasma disk. The fluoropolymer films were exposed to the discharge for two minutes and then allowed to cool for two minutes under a hydrogen atmosphere before exposure to air. Photomodification was accomplished using a XeCl excimer laser. This source provides a beam of 308 nm wavelength with an output power of 25 to 100 mJ per pulse and a pulse width of 35

nanoseconds. The laser was typically operated at a rate of two pulses per second. The films were exposed to from 1 to 500 pulses at focused energy densities between 0.5 and 2.0 J cm<sup>2</sup> pulse. Finally, the electron beam apparatus produces 100 ns pulses of 25-28 KeV electrons with an energy of 2-3 J/pulse. Ten pulses were used for the samples described in this paper.

*Synthesis of the conductive polymer films.* The conductive polymers were synthesized by oxidative polymerizations of the desired monomer [5]. We and others have shown that when such oxidative polymerization are conducted in the presence of a film of an insulating polymer (eg. nylon, polyester, polycarbonate [6-11]) , the insulating polymer becomes coated with a thin, strongly-adherent film of the conductive polymer. This occurs because the rate of polymerization of the conductive polymer is enhanced at the surface of the insulating polymer [6,7]. The thickness of the conductive polymer coat can be varied by varying the polymerization time and polymerization can be quenched by simply removing the coated insulating polymer sheet from the polymerization solution and rinsing. This approach was used in these investigations.

Polypyrrole and poly(N-methylpyrrole) films were synthesized by immersing the fluoropolymer sheet into an aqueous solution prepared by mixing equal volumes of a solution that was 0.1 M in monomer and a solution that was 0.2 M in FeCl<sub>3</sub> and 0.2 M sodium tosylate. Poly(3-methylthiophene) was synthesized from an acetonitrile solution that was 0.1 M in 3-methylthiophene and 0.2 M in Fe(ClO<sub>4</sub>)<sub>3</sub>. Polyaniline was synthesized by mixing equal volumes of a solution that was 0.25 M in ammonium persulfate and a solution that was 0.5 M in aniline; the solvent was 1 M



hydrochloric acid. Reduced forms of poly(N-methylpyrrole) and poly(3-methylthiophene) were obtained by immersing the conductive polymer-coated fluoropolymer sheet into an acetonitrile solution saturated with  $\text{NaBH}_4$ .

## RESULTS AND DISCUSSION

We first show that all four of the surface modification procedures improve adhesion of conductive polymers to fluoropolymer surfaces. We then discuss the chemistry of the various modified fluoropolymer surfaces as assessed by XPS, contact angle measurement and UV-vis-NIR spectroscopies. Finally, we present conductivity and other data on the conductive polymer films coated onto the fluoropolymer surfaces.

*Wet Chemical Method of Improving Conductive Polymer Adhesion.* If an as-received (ie. no surface modification) PTFE or FEP sheet is immersed into a pyrrole polymerization solution (see Experimental), the surface of the membrane *does* become coated with a thin film of polypyrrole. However, this film can be completely removed by simply rubbing the surface with a laboratory tissue. The conductive polymer film can also be removed via the "tape test" [19] whereby a piece of adhesive tape is applied to the surface and then removed. The polypyrrole film is lifted off of the fluoropolymer surface when the tape is removed; ie. the film "fails" the tape test [19]. Clearly, adhesion between the conductive polymer coat and the fluoropolymer substrate is quite poor.

The wet chemical surface modification developed by Shoichet and McCarthy solves this adhesion problem; this is illustrated in Figure 1. This figure shows a

photograph of a piece of FEP film after synthesis of polypyrrole across the film surface. Prior to coating with polypyrrole, the right half of the FEP film was modified using the wet chemical method described above [18]; the left half was not chemically-modified. Polypyrrole was then synthesized across the entire surface and the resulting film was hand-polished with a laboratory tissue. As indicated in Figure 1, the polypyrrole film is completely removed from the unmodified portion of the FEP surface but adheres to the modified portion of the surface. Furthermore, the polypyrrole film was not removed from the modified portion of the surface via application and removal of adhesive tape; ie. the film "passed" the tape test [19]. The increased adhesion to the modified portion of the surface results because this wet chemical method carboxylates the fluoropolymer surface [18] and these carboxylate groups interact electrostatically with the cationic conductive polymer.

The promotion of adhesion between conductive polymers and PTFE can be accomplished by the same wet chemical modification procedure. However, in contrast to FEP, where the initial reduction is surface selective (ie. the depth of the reaction is easily controlled), the reduction of PTFE proceeds corrosively deep into the film [20]. This can potentially result in significant thinning of the PTFE film and increased surface roughness.

*Instrument-Based Methods for Improving Conductive Polymer Adhesion.* In addition to this solution-modification procedure we have investigated several instrument-based methods for modifying the surfaces of FEP and PTFE. As we will demonstrate, these methods also provide improved adhesion of conductive polymers to the

fluoropolymers. We will first briefly describe some of the unique characteristics of each of these instrument-based surface modification procedures. We will then give a more detailed comparison of the chemical and physical effectiveness of each procedure.

Treatment of polymer films with plasmas (or similar corona discharges) is one of the most commonly-used techniques for improving adhesion of polymers to metals [12]. Plasmas contain a number of highly energetic species that can interact with polymers including electrons, radicals, and photons [12]. Hydrogen plasmas have been found to be particularly effective in the surface modification of fluoropolymers [12,21]. The initial modification reaction is thought to be the abstraction of fluorine from the polymer surface by a hydrogen radical [12]. This leaves a radical on the polymer chain that can undergo further reactions such as crosslinking or incorporation of residual oxygen from the plasma. The hydrogen plasma also produces copious quantities of ultraviolet and vacuum ultraviolet photons that are undoubtedly capable of modifying the fluoropolymer [22,23]. It may be noted that the afterglow geometry of the plasma system employed in these studies limits the number of electrons impinging on the sample [15].

Figure 2 shows a photograph of a piece of PTFE film after synthesis of poly(3-methylthiophene) across the film surface. Prior to coating with poly(3-methylthiophene), a circular-shaped portion of the PTFE surface was modified using the hydrogen plasma method described above; the rest of the surface was not plasma-modified. Again the conductive polymer was polymerized over the entire

PTFE surface and the surface was polished with a Kimwipe. After this polishing, the conductive polymer remains only on the circular region of the PTFE-surface that was exposed to the hydrogen plasma. This demonstrates that the plasma treatment is effective in modifying the surface to promote adhesion. Furthermore, this sample also passed the tape test [19].

Electron beam irradiation has also been reported to improve the adhesion of materials to fluoropolymers [14]. Electron beam irradiation has been shown to promote the creation of radicals in PTFE [24-26] which result in cross-linking of the polymer film. We hypothesized that the radicals might also react with oxygen in the electron-beam system leading to the incorporation of oxygen into the fluoropolymer surface that would result in improved adhesion of a conductive polymer coating. This hypothesis is supported by the XPS data presented below. Figure 3 (analogous to Figure 2) demonstrates that improved adhesion is obtained on the electron-beam treated surface.

The final method of fluoropolymer modification attempted in this study was exposure to UV-laser radiation. It has been reported that ultraviolet radiation causes chain scission and crosslinking in FEP [23]. We exposed fluoropolymer films to 308 nm photons from a XeCl excimer laser. Again, we hoped that chain scission would lead to the incorporation of oxygen species into the polymer that would promote adhesion (see XPS data). Figure 4 shows polypyrrole polymerized onto the irradiated surface. For this sample, a mask with groups of several submillimeter holes was placed in the laser beam. Again, initially the entire surface was coated. After

polishing, the polypyrrole only remained on the portion of the surface that was exposed to the UV laser. Note further that this simple experiment demonstrates that it is possible to "write" patterns with conductive polymer on the fluoropolymer surface.

*Characterization of the Modified Fluoropolymer Surfaces.* As discussed above, four methods for modifying fluoropolymer surfaces were investigated. These methods all resulted in improved adhesion between the fluoropolymer films and electronically conductive polymers. To better assess the relative effectiveness of the various techniques in chemically modifying the fluoropolymer surfaces, the modified surfaces were characterized using contact angle measurements, and X-ray photoelectron spectroscopy (XPS). Scanning electron microscopy (SEM) was used to look for changes in fluoropolymer surface morphology caused by the various modification procedures.

Table I shows the effect of the four modification procedures on the advancing contact angle of water on FEP and PTFE. The unmodified fluoropolymers are very hydrophobic and have extremely high contact angles. The contact angles of the modified surfaces are lower than those of the virgin fluoropolymer surfaces. These data clearly show that a higher energy surface is produced by all of the surface modification procedures. This higher surface energy is obviously responsible for the improved adhesion. Based on these contact angle measurements, the surface energy increases in the order virgin surface < laser-treated < solution-modified < electron-beam-treated < plasma-treated. While these contact angle measurements clearly demonstrate that the surfaces of the fluoropolymer films were effectively

modified by the various procedures, contact angle measurements do not provide any information as to what chemical species are present on the surface.

X-ray photoelectron spectroscopy (XPS) was used to investigate the modified surfaces because it provides information on both the elemental composition and the nature of chemical bonding at the surface. Table II shows the elemental composition (as determined by XPS) of the virgin and modified fluoropolymer surfaces. The fluorine content of the virgin fluoropolymers is somewhat lower than theoretically predicted. This is due to residual contamination of the XPS chamber by carbon containing species. [27]. The modified surfaces all show an increase in oxygen content and decrease in fluorine content relative to that of the unmodified surfaces. Hydrogen is undoubtedly incorporated into the fluoropolymer surfaces during some of the modification procedures, particularly during the plasma treatment; however, hydrogen is not directly detectable in XPS. Because hydrogen (and other atoms) were not assayed these are called apparent surface compositions in Table II.

The hydrogen plasma treatment has the greatest effect on the elemental composition of the film surface; exposure to laser photons has the least effect. This agrees qualitatively with the contact angle measurements, where the hydrogen plasma treated surfaces have the lowest contact angles and the surfaces exposed to the UV laser photons have the highest contact angle of any of the modified surfaces. Besides providing the elemental composition of the surface XPS can also provide information about the nature of chemical bonding at the film surface. The C1s binding energy for unmodified fluoropolymers is ca. 292 (Figure 5). This very high carbon

binding energy is caused by the high electronegativity of covalently bound fluorine. In the modified samples a new C1s peak is observed at ca. 284-282 eV (Figure 5). This binding energy is typical of carbon covalently bound to carbon and hydrogen.

The relative intensity of the original (292 eV) and new (282-284 eV) peaks in the C1s spectra is another indicator of the relative effectiveness of the various modification procedures. For the laser-treated surfaces, the original high binding energy peak is dominant with only a small lower binding energy peak present. This indicates that the majority of the carbon at the polymer surface remains in a highly electronegative (fluorine) environment while only a small fraction of the carbon at the polymer surface is in a non-fluorine environment. In other cases (eg. the plasma and e-beam treated surfaces) the original high binding energy peak almost completely disappears. This indicates that the majority of the carbon on the modified surface is in a fluorine-free environment. In summary, both the contact angle measurements and the XPS data (both elemental composition and C1s binding energy) show that the relative effectiveness in chemically modifying of the various procedures is plasma > electron-beam > solution > laser.

In addition to chemically modifying the surface of the fluoropolymers, the four modification procedures could also cause changes in surface roughness. An increase in surface roughness itself, could lead to improved physical adhesion of conductive polymers to the fluoropolymers. The various modified surfaces were therefore examined by scanning electron microscopy. At magnifications of 1000X physical damage of the fluoropolymer could be observed only in the e-beam treated samples

(Figure 6). Some enhancement in surface roughness may be taking place in the other procedures, but was not detectable at this magnification. Higher magnifications did not yield representative pictures because of the inherent surface roughness of the samples.

*Characteristics of the Electronically Conductive Polymer Coatings.* The film thickness, and therefore the surface resistivity and optical density of the conductive polymer coating can be controlled by varying the polymerization time. This is demonstrated for polypyrrole in Table III. Note that surface resistance decreases with polymerization time as a result of the increase in polypyrrole film thickness. It is also possible to control the optical density and surface resistivity by changing the oxidation state of the conductive polymer. This is demonstrated in Figure 7, which shows the UV-vis-NIR spectra of oxidized and reduced forms of poly(3-methylthiophene) on FEP. This ability to chemically or electrochemically control the optical properties might be useful in display devices or electrochromic windows.

Finally, it is interesting to note that copper can be electroplated onto polyaniline [28] and polypyrrole [29]. We also found that copper could be electroplated onto polypyrrole coated fluoropolymers [30]. Fluoropolymers are ideal substrates for electronic devices because of their extremely high resistivity. Selective modification of the host fluoropolymer surface before deposition of the conductive polymer is one way that patterns of conductive polymer can be formed. Note that this patterning (as shown in Figure 4) is accomplished without the use of conventional photoresists. The ability to pattern the conductive polymer coating is an important step in the creation of



electronically conductive polymer based circuits and devices. It is worth noting that in a prior publication we demonstrated, that after deposition, the conductive polymer coating can be patterned via UV laser ablation [31].

## CONCLUSIONS

The adhesion between conductive polymers and fluoropolymers can be improved by modification of the fluoropolymer surface prior to deposition of the conductive polymer. The difference in adhesion between the modified and unmodified surface can be used to pattern the conductive polymer coating. Such coatings have many potential applications.

## **ACKNOWLEDGEMENTS**

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**Table I. Effect of Surface Modification Procedure on Advancing Contact Angle at Surface.**

	Contact Angle (Degrees)	
	FEP	PTFE
Unmodified	114	116
Chemical Modified	99	83
Plasma Modified <sup>1</sup>	67	58
Laser Modified <sup>2</sup>		
5 pulses	102	102
10 pulses	95	97
e-beam modified <sup>3</sup>	79	80

<sup>1</sup> Polymer exposed to hydrogen plasma for 2 minutes.

<sup>2</sup> Polymer irradiated at 308 nm with a XeCl laser with an energy density of 0.5 J/cm<sup>2</sup>/pulse.

<sup>3</sup> Polymer irradiated with 10 pulses of electron-beam.

**Table II. XPS<sup>1</sup> Determination of Apparent Surface Compositions For Modified and Unmodified Fluoropolymer Surfaces.<sup>2</sup>**

Treatment	FEP			PTFE		
	%C	%F	%O	%C	%F	%O
Unmodified	32.88	67.02	0.11	33.49	65.66	0.86
Chemical	63.34	27.94	8.67	39.00	58.46	2.54
Plasma	75.30	11.24	13.46	74.58	13.29	12.13
Laser	32.25	66.67	1.08	42.48	53.91	3.61
e-beam	57.94	26.16	15.91	66.60	19.77	13.63

<sup>1</sup> XPS analysis at a 25 degree takeoff angle.

<sup>2</sup> Modification procedures identical to those in Table I.

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**Table III. Surface Conductivity of Polypyrrole-Coated FEP as a Function  
of Polymerization Time**

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<b>Polymerization Time (Minutes)</b>	<b>Surface Conductivity (Siemens/Square)</b>
1.5	$3.2 \times 10^{-5}$
3	$9.3 \times 10^{-5}$
5	$1.9 \times 10^{-4}$
10	$5.0 \times 10^{-4}$
20	$8.1 \times 10^{-4}$
30	$1.3 \times 10^{-3}$
60	$1.2 \times 10^{-3}$

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## FIGURE CAPTIONS

Figure 1. Photograph of polypyrrole Coated FEP. Right half of FEP was modified prior to coating using the wet chemical procedure. Film was gently hand-polished after pyrrole polymerization.

Figure 2. Photograph of poly(3-methylthiophene) coated PTFE. Circular pattern in center of PTFE surface was exposed to hydrogen plasma. Film was gently hand-polished after 3-Methylthiophene polymerization.

Figure 3. Photograph of polypyrrole coated PTFE. Circular pattern in center of PTFE surface was irradiated with 10 pulses of a soft vacuum electron beam. Film was gently hand-polished after pyrrole polymerization.

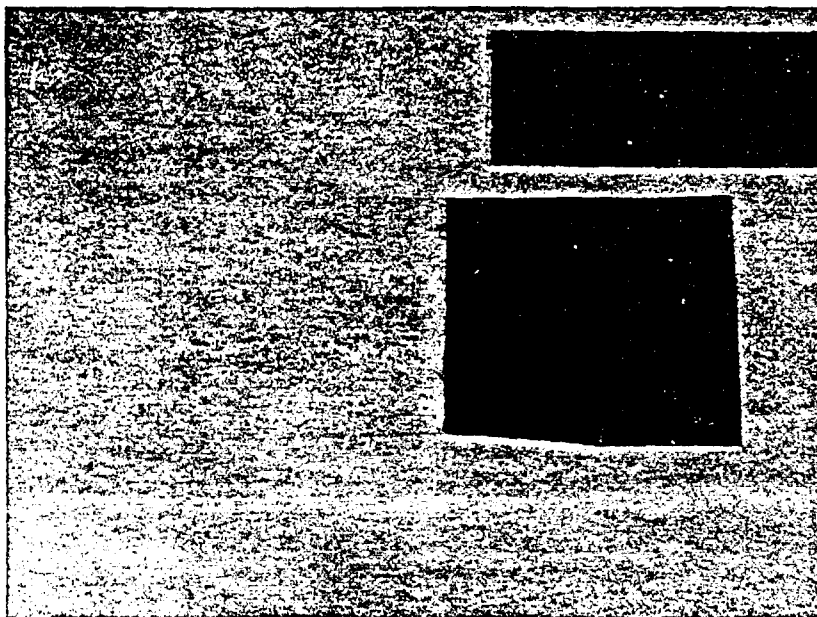
Figure 4. Photograph of polypyrrole coated FEP. Film was irradiated with 308 nm laser light through a mask. Film was gently hand-polished after pyrrole polymerization.

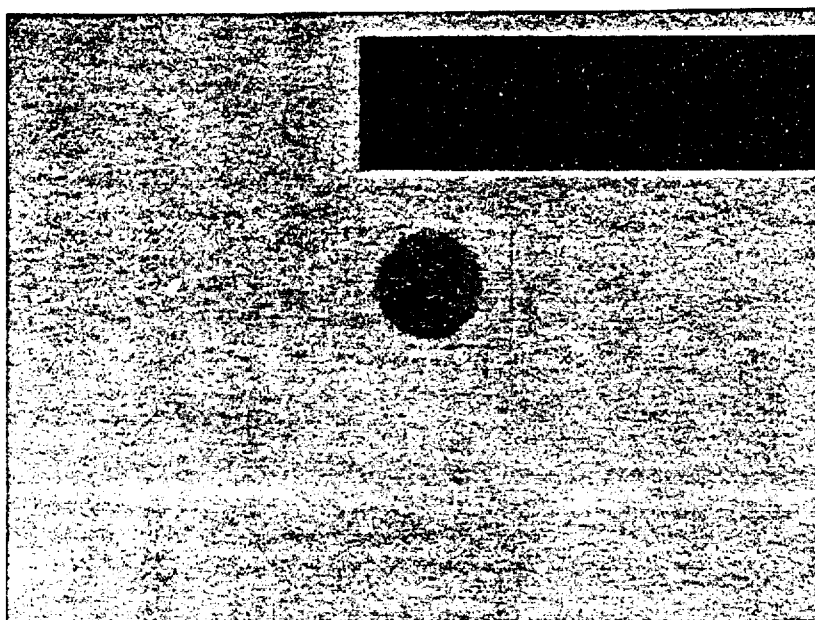
Figure 5. A) C1s XPS spectra of virgin and modified FEP surfaces. B) C1s XPS spectra of virgin and modified PTFE surfaces.

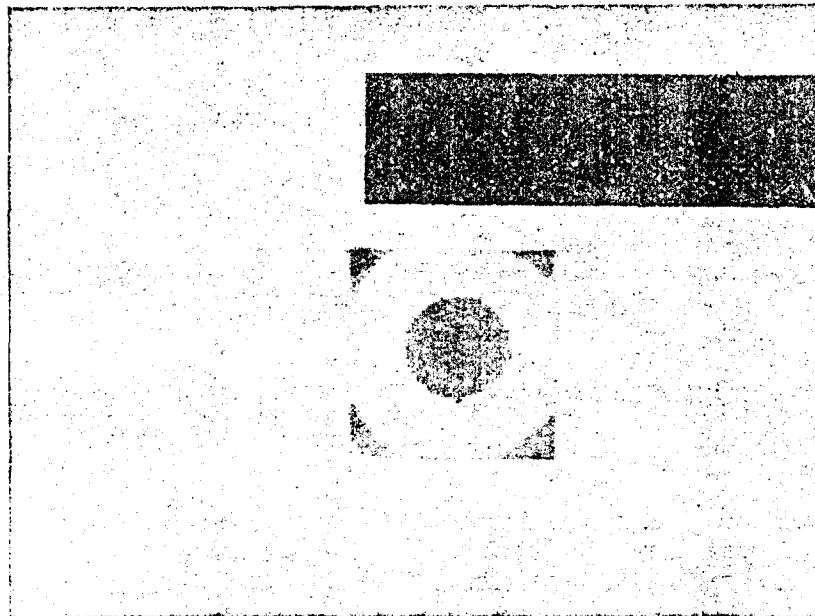
Figure 6. SEM of A) unmodified FEP surface; B) Unmodified PTFE surface. C) High flux electron irradiated FEP; D) High flux electron irradiated PTFE. Note surface damage in C and D occurred only at very high fluxes.

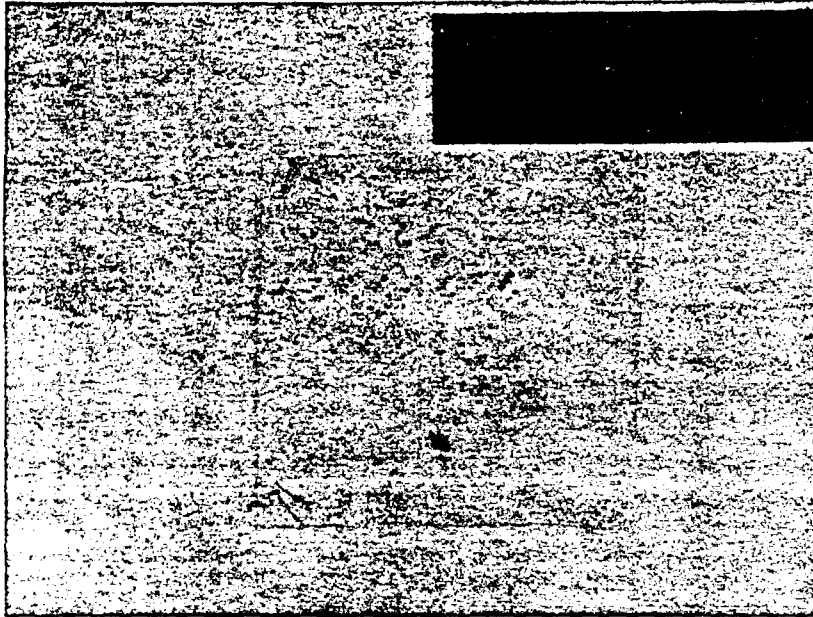
Figure 7. UV-Vis-NIR spectra of FEP coated with oxidized and reduced poly(3-methylthiophene).





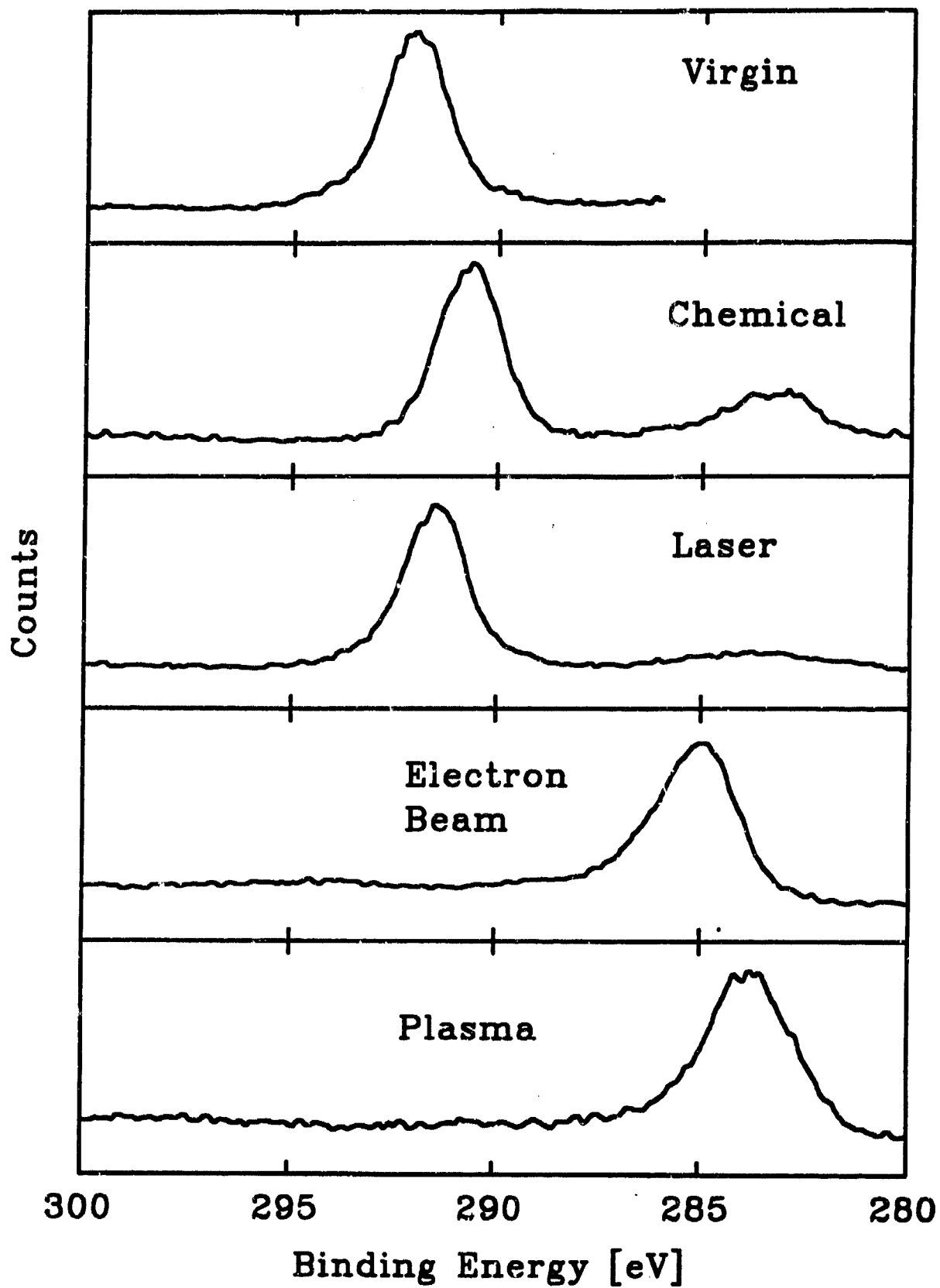




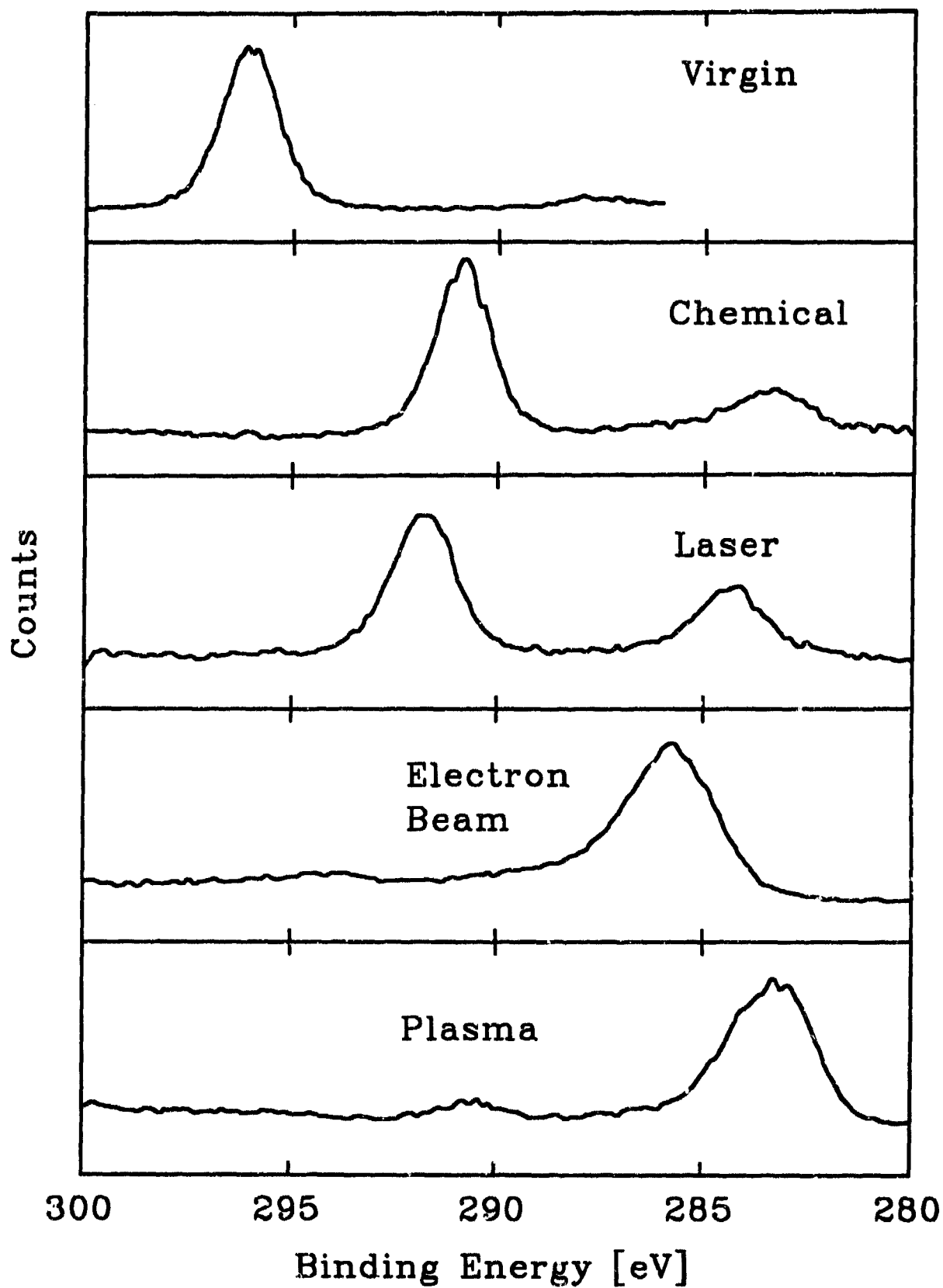


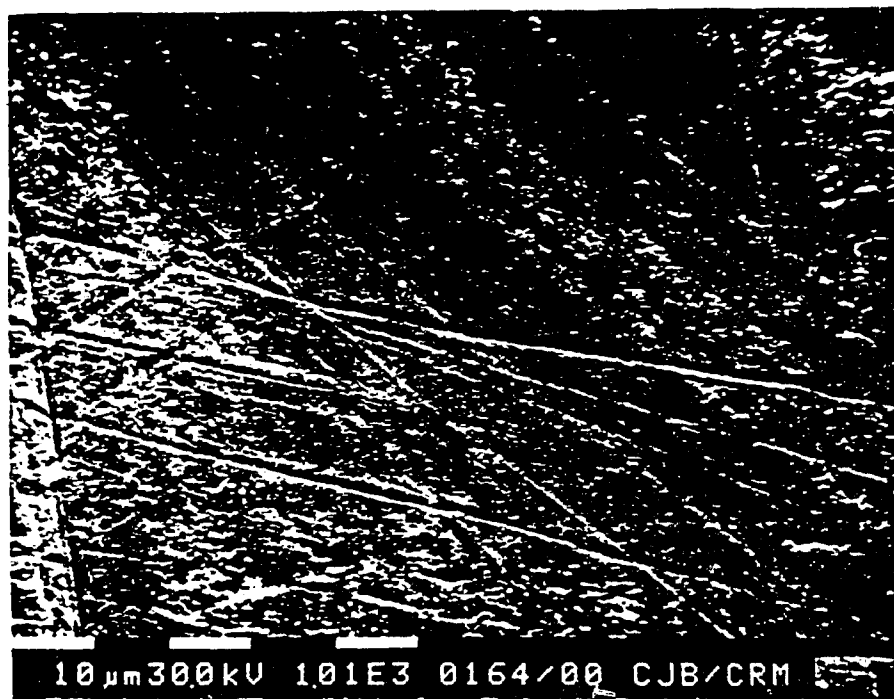
# XPS of FEP Films

5A

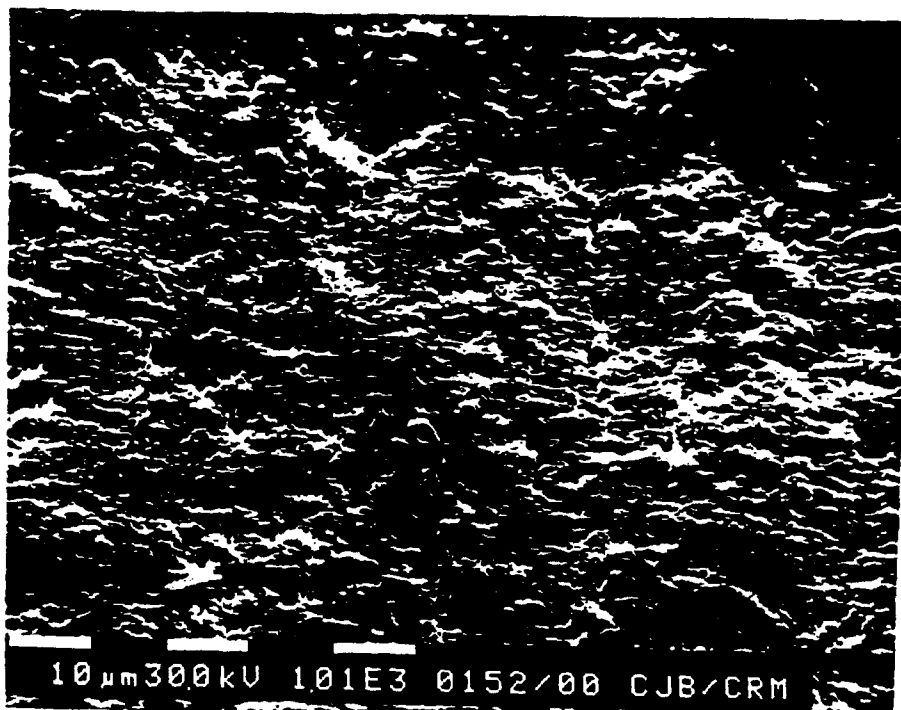


## XPS of PTFE Films

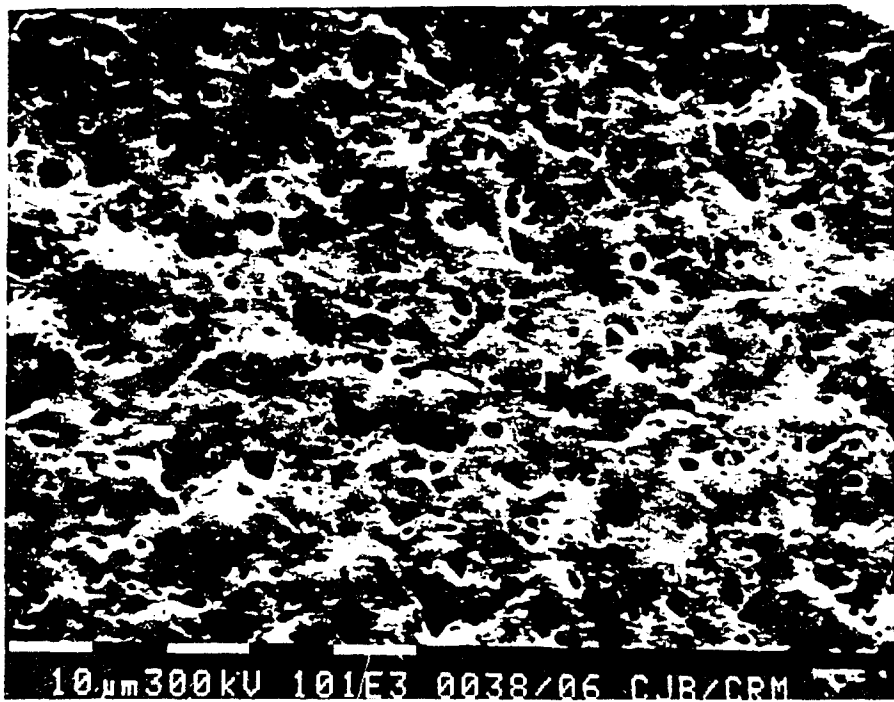




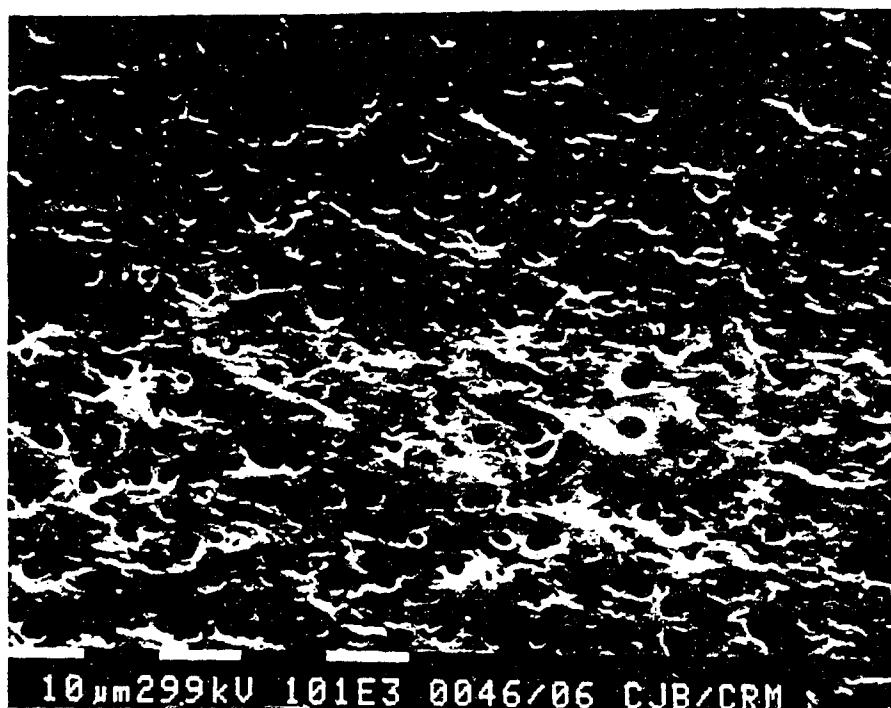
10  $\mu$ m 300kV 101E3 0164/00 CJB/CRM







10  $\mu$ m 300kV 101E3 0038/06 CJB/CRM



10  $\mu$ m 299kV 101E3 0046/06 CJB/CRM

